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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS(U)
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DAJA45-85-C-0023

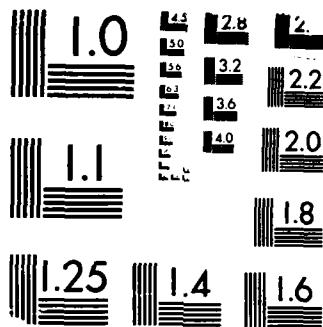
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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS

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Contract n. DAJA 45-85-C-0023

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"Fourth Periodic Report"
August 1986 - January 1987

"The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. ~~This report is intended only for the internal management use of the Contractor and the U.S. Government.~~

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1- Progress of the research

It has been pursued the study on the role of colloidal assemblies in the control of the mechanism and rates of chemical reactions.

The properties and applications of "functionalized" surfactants (in particular with the polar head having complexing capability have been reviewed in order to select proper assemblies for enrichment and catalytic purposes.

The phase separation of non-ionic surfactant solutions above the cloud point can be practically exploited for liquid-liquid extraction of hydrophobic metal-chelate complexes, which can be concentrated in the low volume micellar phase.

A model reaction system consisting of a series of suitable amphiphilic ligands with a tuned alkyl chain (4-alkylamido-2-hydroxybenzoic acids: PAS-C_n, where C_n = R-CO-) and a reactive metal ion (iron (III)) has been investigated in the presence of non-ionic Brij 35 micelles. The formation of 1:1 complexes in acidic solution has been assessed and the corresponding apparent formation constants have been determined using the usual spectrophotometric techniques.

The effect of the micellar system on the ligand acid-base equilibrium has been also investigated and, from the variation of the pK_a values with surfactant concentration and from micellar HPLC measurements, the binding constants of the ligands to the aggregates have been evaluated.

The kinetics of complex formation, studied using the stopped-flow technique, is still fast, even in the presence of relevant concentrations of micellized surfactant, then this step cannot be considered rate-determining in the phase separation procedure.

On the basis of the above preliminary data, collected for the compounds PAS-C_n with n = 2, 4 and 7, a threshold value for the ligand binding constant of ca. 1000 M^{-1} has been determined in order to have a suitable binding of the corresponding iron(III) complexes to the micelles.

Then, extraction of iron(III) has been achieved using a non-ionic surfactant mixture having a proper cloud point, not far from the room temperature range, and good solubilizing capability towards the ligands

and their complexes. Aqueous solutions of Triton X 100 and polyoxyethylene(4.2)dodecanol, both in the range 0.5 - 2% w/v, have been successfully used. The corresponding cloud temperatures are between 26° and 29°C, so that the system readily separates in two phases upon slight heating (ca. 35°C). The addition of inert salt (NaNO₃ 5 - 10% w/v) facilitates fast centrifugation.

The experiments have been performed at a fixed pH (2 - 4) and the amount of extracted iron(III) in the deep violet micellar-rich phase has been shown to be dependent on ligand hydrophobicity. For example, a quantitative recovery (99.9%) of the metal ion in a single extraction step has been obtained at pH 3.5 using PAS-C12.

Further analytical and catalytic developments of these multiphase extraction systems are presently under investigation.

Finally, the previously demonstrated efficiency of semiconductor powders in degradation and complete mineralization of haloaromatic compounds, has been applied to the disposal of sparingly water-soluble pollutants.

Thus DDT, PCB and dioxins have been exposed to irradiation under simulated solar light in aqueous oxygenated solutions containing suspensions of semiconductor particles. TiO₂ was shown to be the most effective, reducing for example the half-life of DDT to about 1 hour.

Since chloride ions are formed in almost stoichiometric yield and no DDE or DDD have been detected by GC, the mechanism is thought to act by hydroxyl radical attack to the benzene rings, with subsequent ring opening.

The potential applicability of the process to degradation of environmental pollutants has been stressed.

References

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2- Research plans

-Photodegradation of organic compounds by visible light.

Other haloaromatic and heteroaromatic compounds will be considered.

Particular attention will be devoted in the investigation of the details of the reaction mechanism (adsorption-desorption process, kinetics, inhibition, nature of the semiconductor and its surface, detection of intermediates. Heterostructured materials (iron oxides onto TiO_2) and titanates will be investigated as photocatalysts.

-The kinetics and mechanism of oxidation of organic compounds in the presence of organized assemblies, such as micelles and microemulsions, will be explored with particular attention to catalytic processes. The preparation of aggregates with reactive components will be pursued.

-The effect of solvent composition on electron transfer reactions will be examined. Oxidation of benzenediols in water/organic solvent mixtures will be investigated.

-The physico-chemical properties of colloidal aggregates will be investigated, with particular attention to functionalized surfactants. Detergents with polar heads exhibiting complexing as well as electron transfer properties will be considered.

3- No significative administrative actions occurred during the period reported.

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6- The funds of the third instalment are now available.

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